Electrodeposited TEOS (tetraethyl orthosilicate) as a pretreatment for organic coating on AA 1100 aluminum sheets

Vitor Bonamigo Moreira[a], Álvaro Meneguzzi[b], Jane Zoppas Ferreira[c]

Abstract

Silane-based coatings are a promising possibility for substituting chromate conversion coatings on aluminum, once their efficiency as pretreatment for panting has already been proved. The most common technique used in order to obtain such coatings is currently the dip-coating on silane sol-gel, which may result in non-homogeneous films, weakening their barrier capacity for corrosion protection. Such difficulty may be overcome with the use of silane electrodeposition. Despite its usual denomination, silane electrodeposition doesn't consist on reduction of a ionic species over the surface. It is better described as a surface activation due to water electrolysis. In this study, TEOS coatings were produced by electrochemical technique over aluminum surface using different overpotentials, with the samples eventually receiving organic coating of nitrocellulose resin. These electrodeposition coatings were compared to dip-coating obtained ones after painting. Both coatings were tested comparatively by electrochemical impedance spectroscopy, potentiodynamic polarization, salt spray and paint adherence tests. The coatings were also compared to chromate-based conventional coatings. The results show a promising technology to the achievement of efficient and environmentally friendly coatings.

Keywords: Silane, Electrodeposition, Aluminum, Organic coating, Pretreatment

Introduction

The efficiency of chromate conversion coatings on corrosion protection, paint or adhesive bonding, makes them largely used as pretreatment for painting or as final coatings (1). The main issue regarding the use of these coatings lies on the toxicity and carcinogenic risk of the Cr^{+6} ion (2), which has already induced heavy regulation of its use and waste by environmental legislation (3).

This stimulates the search for equally efficient and environmentally friendly alternatives for chromate conversion coatings, and this context favors the use of silane coatings. The protection provided by silane coatings is obtained by forming a silane layer that acts as a barrier that keeps the metal from the electrolyte. With the lack of further protection

---

[a] Materials Engineer – Laboratório de Corrosão, Proteção e Reciclagem de Materiais/UFRGS
[b] PHD, Professor – Laboratório de Corrosão, Proteção e Reciclagem de Materiais/UFRGS
[c] PHD, Professor – Laboratório de Corrosão, Proteção e Reciclagem de Materiais/UFRGS

mechanisms, the silane coatings protection depends on the film integrity and coherence, largely influenced by the nature and preparation of the metallic surface. (4)

The standard application method for silane coatings is currently the dip-coating in hydroalcoholic solution, once it is the simplest and cheapest one. However, this technique may produce non-uniform silane coatings, leading to poor corrosion protection. In the other hand, it is believed that electrodeposition may provide more uniform and crosslinked silane coatings (5).

The so called electrodeposition of silanes, explored in this survey, isn't actually a silane deposition in the traditional molds of metallic ions electrodeposition by its reduction on the cathode. The most plausible hypothesis is that the OH- concentration increases over the cathode (5), which favors the formation of hydrogen bonds between the silane and the metallic surface. Nevertheless, due to the consolidation of its use, the procedure will be referred as "electrodeposition".

For this survey, aluminum has been chosen as a substrate because it is widely used as one of the main structural materials in many different projects, and chromate conversion coating is the usual pretreatment for painting it. TEOS (tetraethyl orthosilicate) is a non-functionalized silane, and its availability and relatively low cost makes it an interesting material for a technological use.

The objective of this survey is to validate the efficiency of the electrodeposition technique for silanes comparing it to traditional dip-coating and, in addition, compare it to traditional chromate based treatments.

Experimental

Reagent grade 98% Sigma-Aldrich TEOS was dissolved in hydroalcoholic solution in the following volume ratio: 4% TEOS / 48% distilled and deionized water / 48% ethanol 96%. The pH was set to 2,5 using acetic acid and the solution remained 24 hours under stirring at room temperature for hydrolysis.

AA 1100 aluminum sheets (100 mm x 50 mm x 0,5 mm) were used as metallic substrates for the produced coatings. The sample preparation followed the steps described below and shown in Figure 1.

a) Degreasing: the samples were initially cleaned with a cloth soaked in acetone and then immersed in a commercial alkaline degreasing (Saloclean 667N) solution at 70° C for 10 minutes. Blank samples were painted right after this procedure;

b) Dip-coating: the samples were immersed, using Marconi Dip-Coating equipment, in the silane hydroalcoholic solution for 5 minutes and then removed from immersion with a constant rate of 210 mm/min;

c) Electrodeposition: three overpotentials (+0,4 V, -0,2 V and -0,6 V relative to OCP, measured for each sample) were applied for 5 minutes in silane electrodeposition using an Ag|AgCl reference electrode and stainless steel counter electrodes in a three-electrode conventional cell;

d) Drying: excess liquid from coated surfaces was dried at 50° C for 10 minutes;

e) Curing: curing occurred at 125° C for 1 hour for all samples;

f) Chromate: 5 minute immersion in a chromate solution containing Na_2S, CrO_3 and NaCl;

g) Painting: painting with commercial alkyd varnish was obtained by dip-coating with a Marconi Dip-Coating equipment with constant removal rate of 420 mm/min. The varnish viscosity was maintained constant. All samples were painted for all the analysis performed in this work, except for energy dispersive spectroscopy (EDS).
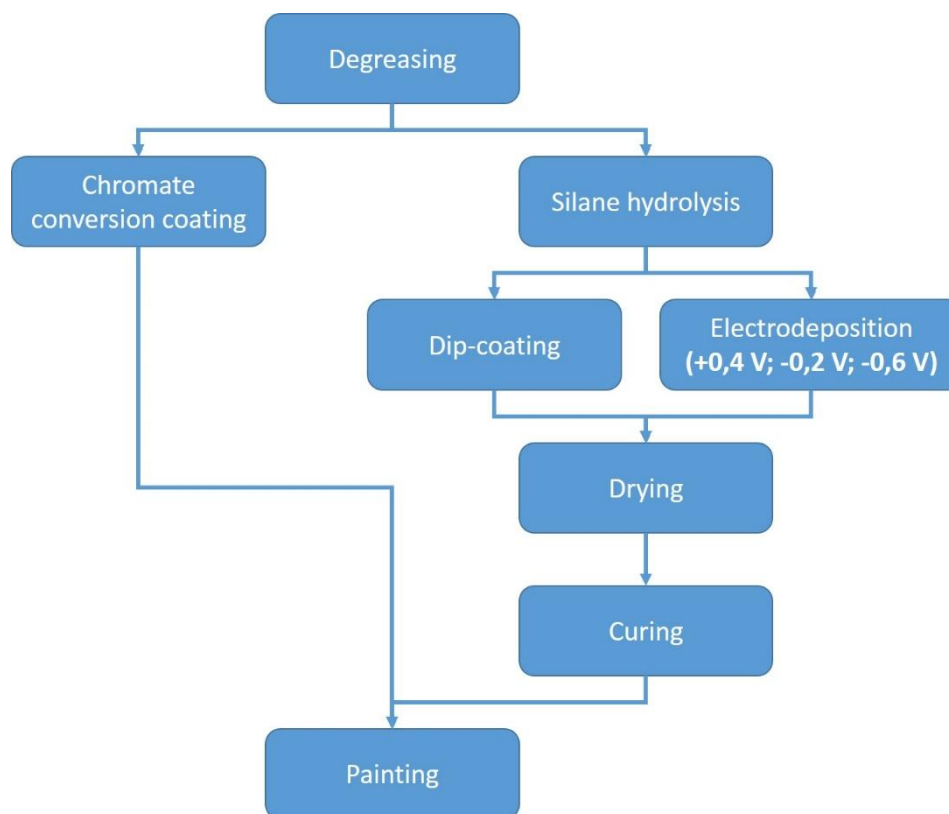
```
                    ┌──────────────┐
                    │  Degreasing  │
                    └──────┬───────┘
          ┌────────────────┴──────────────────┐
 ┌──────────────────┐              ┌──────────────────┐
 │     Chromate     │              │ Silane hydrolysis│
 │ conversion coating│             └────────┬─────────┘
 └──────────────────┘            ┌──────────┴──────────┐
                        ┌─────────────┐   ┌────────────────────────┐
                        │ Dip-coating │   │   Electrodeposition    │
                        └──────┬──────┘   │ (+0,4 V; -0,2 V; -0,6 V)│
                               │          └───────────┬────────────┘
                               │          ┌───────────────┐
                               │          │    Drying     │
                               │          └───────┬───────┘
                               │          ┌───────────────┐
                               │          │    Curing     │
                               │          └───────┬───────┘
                       ┌───────────────┐
                       │   Painting    │
                       └───────────────┘
```

Figure 1. Flowchart of sample preparation procedure.

In order to define the electrodeposition potentials to be used and identify corrosion potential, a cyclic voltammetry was made from -2 V to 0,5 V using an Ag|AgCl reference electrode in the silane solution previously described.

The corrosion protection properties of coatings were measured by electrochemical impedance spectroscopy (EIS) in an area of 0,63 cm^2 with frequencies from 10^6 to 10^{-1} Hz and AC excitation amplitude of 10 mV, using Ag|AgCl reference electrode and platinum counter electrode in AUTOLAB PGSTAT 302 running Nova 1.11 software, after contact for 3 and 24 hours in cells filled with 0,1M NaCl solution. Corrosion rate was estimated based on potentiodynamic polarization tests, carried out with the same equipment and software from EIS, after 1 hour of cell mounting. The adopted scan rate was 0,004 V/s, and the scan range was from +0,5 V to -0,5 V relative to OCP. Salt spray tests were carried according to ASTM B117 and the painted samples were evaluated using ASTM D610 standard.

Paint adhesion was measured by both ASTM D3359 and ASTM D4541 standards.

The coatings' flexibility was assessed by mandrel bend test according to ASTM D522.

A Zeiss EVO MA10 device was used for EDS analysis. An element mapping was carried out for each sample by EDS, in order to evaluate the proportion of surface covered by silicon, which indicates the presence of the silane coating. The covered area percent was then calculated with ImageJ software.

Results and discussion

Voltammetry

Figure 2 is a voltammogram with the same electrodeposition solution and electrodes held with the scope of defining the electrodeposition potentials and observing corrosion behavior related to the scanned potentials.
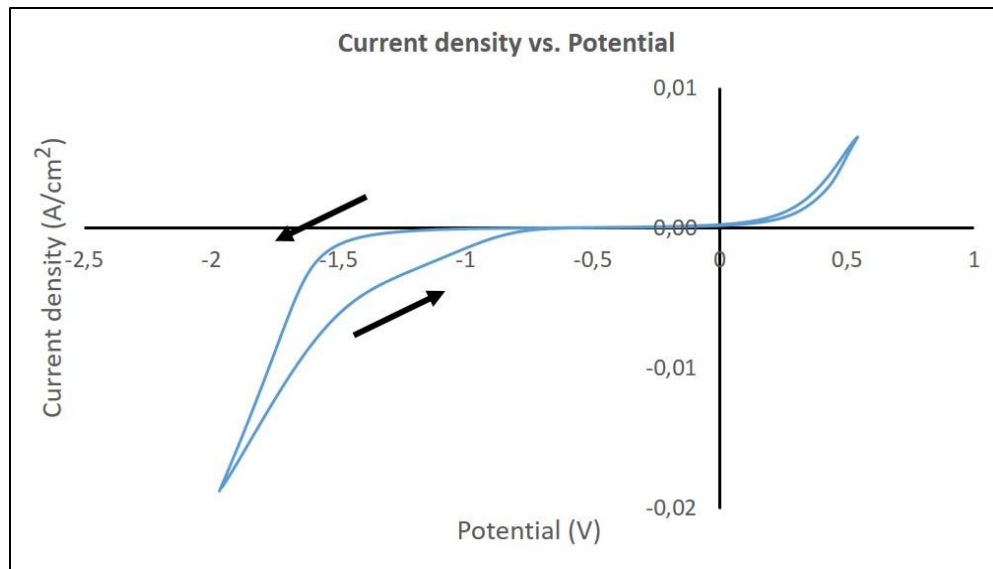

Figure 2. Voltammogram with potential scan from -2 $V_{Ag|AgCl}$ to +0,5 $V_{Ag|AgCl}$, at scan rate 0,004 V/s, for AA 1100 aluminum sheet in 4% TEOS / 48% water / 48% ethanol with pH set to 2,5 using acetic acid.

The scan resulted in cathodic current below approximately -0,57 $V_{Ag|AgCl}$ and anodic current above this potential. Two cathodic potentials [OCP + (-0,6 $V_{Ag|AgCl}$) and OCP + (-0,2 $V_{Ag|AgCl}$)] and one anodic potential [OCP + (+0,4 $V_{Ag|AgCl}$)] were chosen for electrodeposition. The cathodic potentials were chosen to promote the OH- generation on the metallic surface, while the anodic potential was used to test this hypothesis.

Besides that, none of the scanned potentials resulted in a drastic increase of the current density, indicating that there was no disproportional acceleration of corrosion in consequence of the applied potentials.

Electrochemical impedance spectroscopy

EIS analysis were conducted in a three-electrode cell containing the coated surface as the work electrode, a reference Ag|AgCl electrode and a platinum counter electrode. The obtained results for 3 hours and 24 hours after mounting and filling the cells with 0,1 M NaCl are plotted in Nyquist diagrams in Figure 3 and Figure 4, respectively.
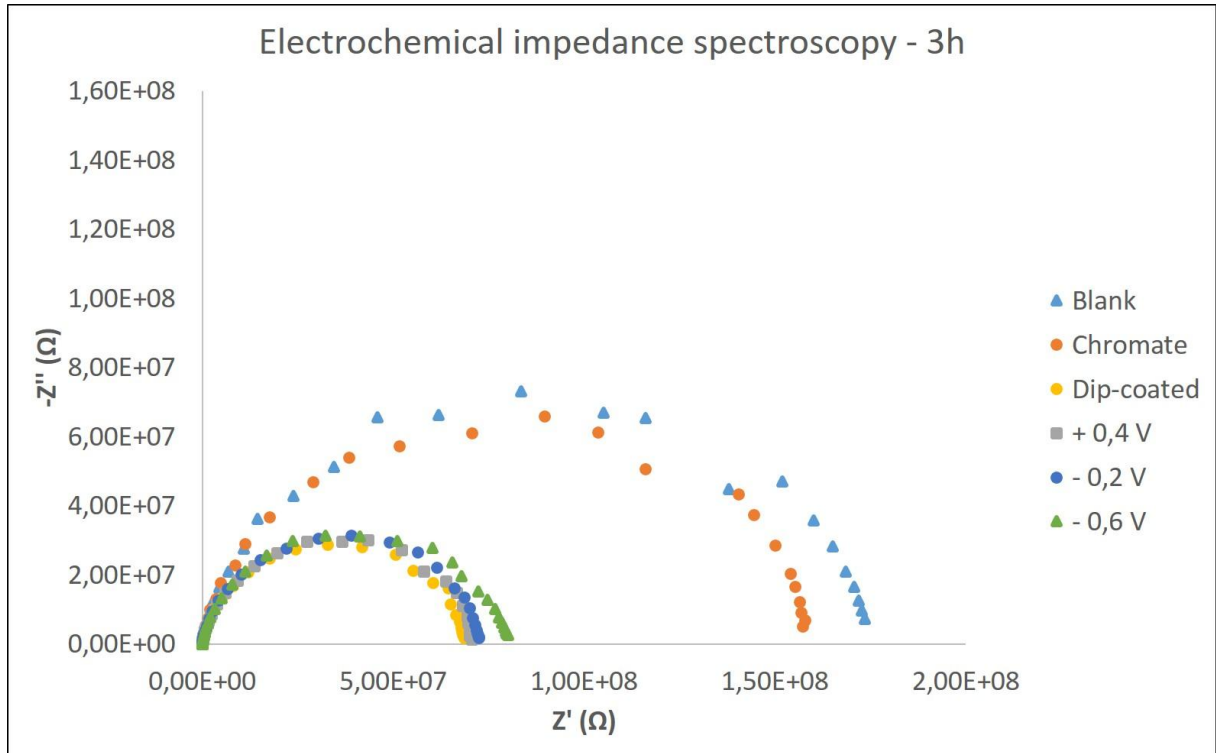
Figure 3. **Nyquist diagrams for blank, chromate coated and silane coated samples 3 hours after cell mounting with Ag|AgCl reference electrode, Pt counter electrode and 0,1 M NaCl electrolyte. DC excitation of 10mV from 10^6 Hz to 10^{-1} Hz.**
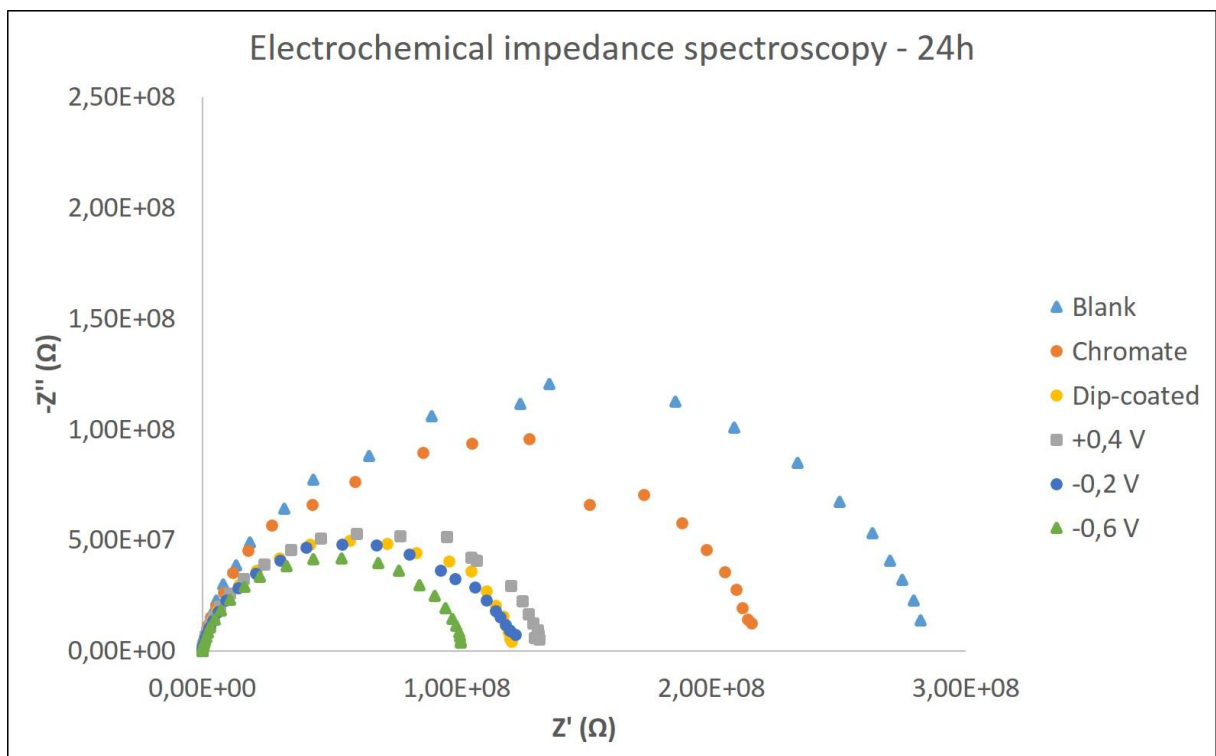

Figure 4. Nyquist diagrams for blank, chromate coated and silane coated samples 24 hours after cell mounting with Ag|AgCl reference electrode, Pt counter electrode and 0,1 M NaCl electrolyte. DC excitation of 10mV from 10^6 Hz to 10^{-1} Hz.

It can be noticed that silane coatings showed lower corrosion protection compared to blank

and chromate samples. It is also evident that, from 3 hours to 24 hours of exposure to the electrolyte, all of the samples showed an increase in impedance values, which is probably a consequence of the growth of an aluminum oxide layer. It is possible that the presence of silane coatings hindered that growth by partially avoiding the contact between substrate and electrolyte.

Corrosion rate
The corrosion rates, calculated from potentiodynamic polarization, are shown in Table 1.

Table 1. Average and standard deviation of corrosion rate for painted aluminum sheets.

Sample pretreatment	Average corrosion rate (± standard deviation) (mm/year)
Blank	$2,5 \times 10^{-5}$ ($\pm 5,2 \times 10^{-6}$)
Chromate	$3,1 \times 10^{-5}$ ($\pm 1,2 \times 10^{-5}$)
Dip-coating	$1,9 \times 10^{-5}$ ($\pm 9,0 \times 10^{-6}$)
+0,4 V electrodeposition	$2,3 \times 10^{-5}$ ($\pm 1,0 \times 10^{-5}$)
-0,2 V electrodeposition	$2,7 \times 10^{-5}$ ($\pm 5,6 \times 10^{-6}$)
-0,6 V electrodeposition	$2,5 \times 10^{-5}$ ($\pm 1,7 \times 10^{-5}$)

All of the samples have shown similar corrosion rate. This may be an indicative that the alkyd varnish used for this comparison provides good corrosion protection, masking the differences between the analyzed pretreatments.

Salt spray test
After 480 hours of exposure to salt spray, none of the samples showed corrosion, which represents corrosion grade 10. Therefore, by this analysis it was not possible to detect any difference of corrosion protection provided by the tested pretreatments.

Paint adhesion
Table 3 shows the measures for paint adhesion by tape test and pull-off using portable adhesion tester.

Table 3. Paint adhesion measured for the studied pretreatments according to ASTM D3359 and ASTM D4541.

Sample pretreatment	Paint adhesion ASTM D3359	Average paint adhesion (± standard deviation) (MPa) ASTM D4541
Blank	4B	1,40 (± 0,16)
Chromate	4B	1,42 (± 0,13)
Dip-coating	3B	0,85 (± 0,16)
+0,4 V electrodeposition	3B	1,04 (± 0,01)
-0,2 V electrodeposition	3B	0,70 (± 0,11)
-0,6 V electrodeposition	3B	0,82 (± 0,18)

Both testing methods indicate that the TEOS coating, either by dip-coating or by electrodeposition, didn't improve paint adhesion on the aluminum sheets. This result is not surprising, once TEOS is not a functional silane, therefore it lacks of chemical functions which could have promoted chemical bonding between the silane layer and the organic coating. This kind of chemical interaction in order to promote adhesion may be obtained by using a functionalized silane.

Flexibility test
The bending test on conic mandrel, described in ASTM D522 standard, did not result in cracks or loss of adhesion of the organic coating. This can be seen in Figure 5.
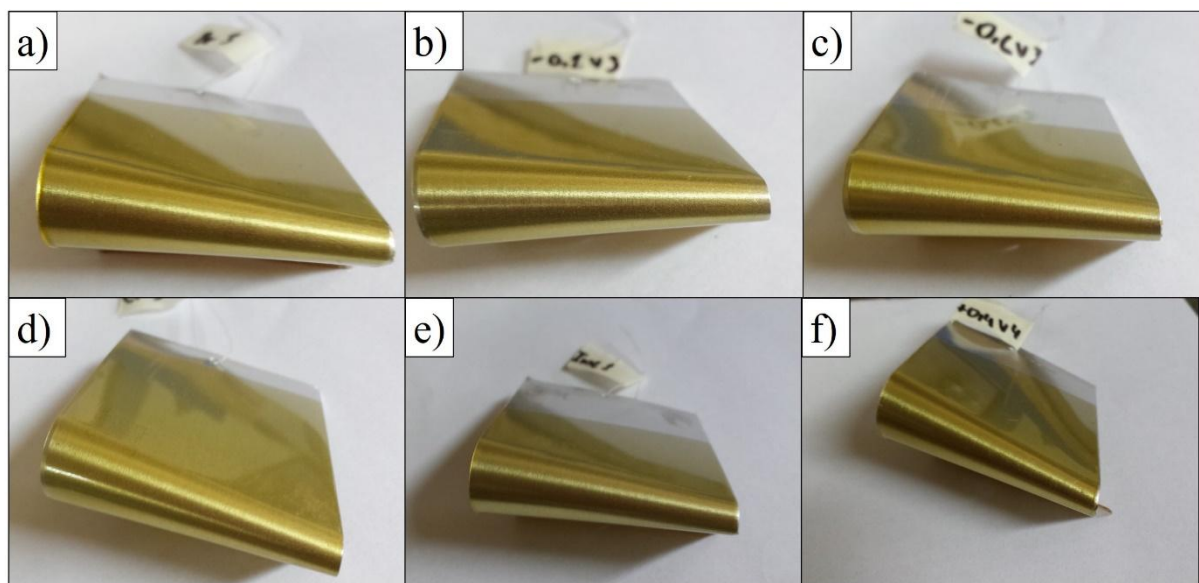

Figure 5. Samples after bending in the smallest extremity of the conic mandrel.

a) Blank; b) -0,2 V; c) -0,6 V; d) Chromate; e) Dip-coated; f) +0,4 V.

All samples have gone flawlessly through a 32% elongation, which is the maximum elongation imposed by the equipment, showing that the flexibility of the organic coating has not been impaired by the used pretreatments.

Energy dispersive spectroscopy
The silicon mapping for the analyzed samples resulted in the images compiled in Figure 6. The black areas indicate the absence of silicon, and white and grey areas indicate its presence, which is an indicative of silane coating formation.
Table 4 contains the proportional area where silicon was detected for each sample.

Table 4. Area percent containing silicon, calculated using ImageJ software, for pretreated non-painted samples.

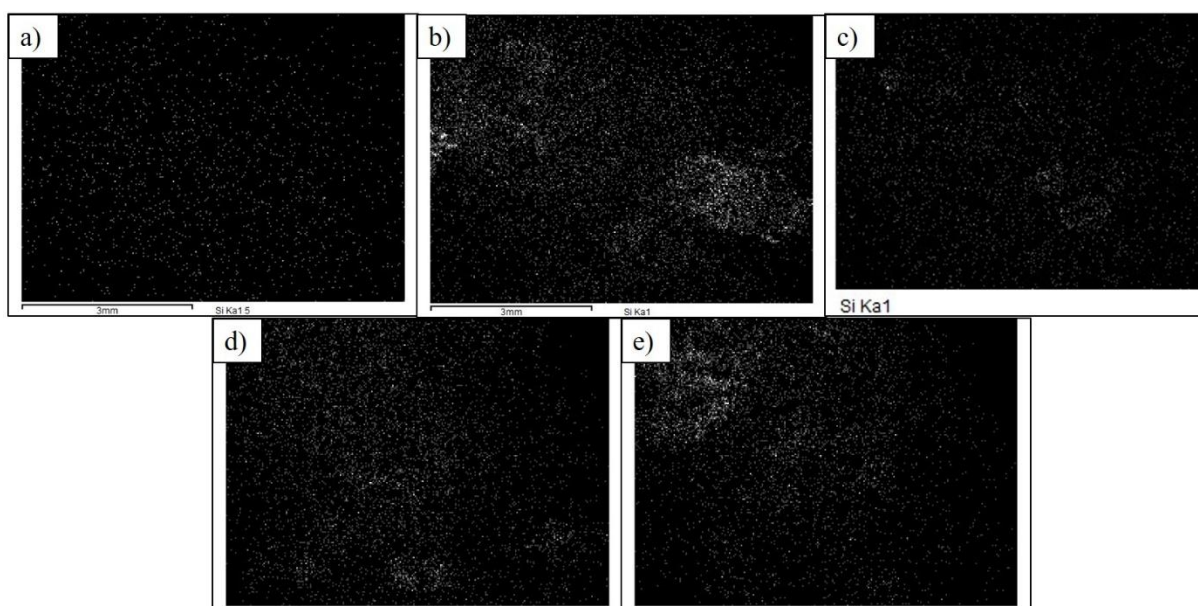| Sample pretreatment	Area percent containing silicon (%)
Blank	3,34
Dip-coating	15,73
+0,4 V electrodeposition	6,13
-0,2 V electrodeposition	40,88
-0,6 V electrodeposition	36,37

Figure 6. Silicon maps obtained by EDS for a) Blank, b) Dip-coated, c) +0,4 V electrodeposition, d) -0,2 V electrodeposition and e) -0,6 V electrodeposition. White and grey dots indicate the occurrence of silicon, evidence of silane presence.

The maps from Figure 6 show the non-homogeneous distribution of silicon over the aluminum surface for the dip-coated sample, which corroborates the hypothesis that this coating technique may lead to non-homogeneous layers. The light colored areas indicate a higher concentration of the element, confirming difference of silane distribution over the surface resulting from dip-coating technique.

The comparison of the proportional areas containing silicon indicates that electrodeposition in cathodic potentials leaded to a better distribution of silane along the surface, while anodic potentials resulted in minimum coverage of the surface. This is a strong evidence that the electrodeposition in cathodic potentials may act as a surface activation, increasing the OH^- concentration along the substrate surface by water electrolysis and generating more active sites for silane linkage, providing greater coverage of the substrate.

Conclusions

The voltammetry carried out with the electrodeposition cell showed the absence of disproportional increase of current density, indicating that none of the scanned potentials would accelerate drastically the corrosion of the substrate.

Electrochemical impedance spectroscopy analysis showed that TEOS coatings did not improve the corrosion protection of aluminum. The impedance has increased for all samples from 3 to 24 hours, which may be a consequence of the growth of an oxide layer over the surface. It is possible that silane coatings hindered this growth.

The corrosion rate for all pretreatments was similar. This may be an indicative that the varnish used for painting all the samples provided good corrosion protection, masking possible differences between the tested pretreatments.

Salt spray test has not shown any difference on corrosion protection of the tested pretreatments, once all of them remained without any corrosion during the time that the test was performed.

Both methods of paint adhesion measurements resulted in a decrease in paint adhesion for TEOS coated samples, either by dip-coating or by electrodeposition. TEOS is a non-functional silane, so it is not expected to promote paint adhesion. The use of an organofunctional silane could overcome this issue.

The organic coating's flexibility has not been impaired by any of the used pretreatments. The testing method indicated that for all samples the elongation of 32% did not result in cracking or loss of adherence of the varnish.

The EDS silicon mapping provided important results, once it illustrated the non-homogeneous coverage capacity by the dip-coating method. Besides that, the electrodeposition of silane resulted in a greater area containing silicon, which confirms the efficiency of this technique for obtaining films that are more homogeneous.

References

(1) **Eppensteiner, Fred and Jenkins, Melvin R.** Chromate conversion coatings. *Metal Finishing.* 10, 2007, Vol. 105.

(2) **U.S. Department of Health and Human Services.** *Toxicological profile for Chromium.* Atlanta : s.n., 2012.

(3) **Pommiers, S., et al.** Alternative conversion coatings to chromate for the protection of magnesium alloys. *Corrosion Science.* 84, 2014.

(4) **Van Ooij, W. J., et al.** Corrosion protection properties of organofunctional silanes - An overview. *Tsinghua Science and Technology.* 2005, Vol. 10.

(5) **Gandhi, J. S.** *Electrodeposition of organofunctional silanes for improved corrosion protection of metals.* s.l. : University of Cincinnati, 2004.